STUDIES ON HYDROLYTIC OXIDATION OF ORGANOSILANES WITH GOLD NANOPARTICLE - BASED PICKERING CATALYSTS - SYNTHESIS AND REACTIVITY OF 1,1,3,3-TETRAORGANODISILOXANES

ASMITA SHARMA

DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY DELHI

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by

ASMITA SHARMA

Department of Chemistry

Submitted

In fulfillment of the requirements of the degree of Doctor of Philosophy

to the

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Dedicated to My Family

CERTIFICATE

This is to certify that the thesis entitled "**S*tudies on hydrolytic oxidation of organosilanes with gold nanoparticle-based Pickering catalysts - Synthesis and reactivity of 1,1,3,3-tetraorganodisiloxanes***" being submitted by **Ms. Asmita Sharma** to the Department of Chemistry, Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy** is a record of bonafide research work carried out by her.

Asmita Sharma has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results contained in this thesis have not been submitted in part or in full to any other University or Institute for the award of any degree or diploma.

Prof. Ravi Shankar

Department of Chemistry,
Indian Institute of Technology Delhi,
New Delhi-110016, India.

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ABSTRACT

The work embodied in the thesis provides a systematic study to develop Au nanoparticle-based Pickering interfacial catalysts (PICs) and their application for hydrolytic oxidation of secondary organosilanes to afford the synthesis of 1,1,3,3-tetraorganodisiloxanes, $(HRR^1Si)_2O$ (R, R^1 = alkyl/ aryl). During the course of this work, we have examined plasmon-induced photothermal effect arising from excitation of surface plasmon resonance of AuNPs under visible light irradiation and its implication in the catalytic reactions under study. The thesis is divided into five chapters. Chapter I provides an overview of literature dealing with the synthesis and reactivity of linear/ cyclic organosiloxanes bearing Si-H/ Si-vinyl/ Si-OH/ Si-OR groups. Chapter II relates to a detailed description of synthetic procedures and characterization methods being followed in the present study.

In chapter III, the study provides a simple and viable approach to construct AuNP-based Pickering interfacial catalysts. The method relies upon initial synthesis of AuNPs tethered with cyclic $[RSCH_2CH_2SiMeO]_4$, [R = CH_2CH_2OH (**1**); CH_2CH_2COOH (**2**)] in chloroform. Upon addition of water, the NPs undergo a spontaneous phase transfer from organic layer to water-chloroform interface. This phenomenon is evident by the formation of non-coalescent water droplets dispersed in chloroform. The biphasic systems thus formed are designated as Pickering interfacial catalysts, **PIC-1** and **PIC-2**. Chapter IV is devoted to a detailed study on the efficacy of the Pickering catalysts towards hydrolytic oxidation of organosilanes. As a case study, the reaction of methylphenylsilane was performed with 0.01 mol % of Au (**PIC-1**) catalyst by varying the conditions as: 25 °C (dark, ambient light and 680 nm LED source) and 80 °C (dark and ambient light). While the catalyst is found to be inert in the absence of light at 25 °C, the reaction proceeds smoothly upon illumination with ambient light as well as 680 nm LED source. A significant

increase in the catalytic activity is observed at elevated temperature (80 °C). The results suggest that the activity of the NPs at 25 °C is enhanced by photo-induced phenomenon (photothermal effect) which results from plasmon excitation of AuNPs under light irradiation. It is well-known that an underlying mechanism of plasmonic catalysis involves efficient conversion of the absorbed energy into heat, resulting in elevated temperature in the vicinity of the nanoparticles. The catalyst is found to be selective to afford the formation of 1,3-dimethyl-1,3-diphenyldisiloxane, $(HMePhSi)_2O$, as the major product alongwith minor amount (< 5%) of $MePhSi(OSiMePhH)_2$. The method finds a wide substrate scope and offers a promising route for the synthesis of various 1,1,3,3-tetraorganodisiloxanes, $(HRR^1Si)_2O$, ($R = Me, Ph$; R^1 = Ph, *n*-Hex, *n*-Oct, cyclohexyl, $PhMe_2SiCH_2CH_2$, 2-$ThMe_2SiCH_2CH_2$; Th = thienyl). The Pickering interfacial catalyst **PIC-2** is relatively less stable during the catalytic event. In a follow up study, we have examined the reactivity of $(HMePhSi)_2O$ and $(HPh_2Si)_2O$ towards hydrosilylation as well as dealkylative coupling reactions with appropriate substrates. The study has led to the synthesis of functionally-substituted disiloxanes as well as linear oligosiloxanes bearing varying substituents on the silicon atoms. The work presented in chapter V deals with the synthesis of siloxane-modified polyisobornylmethacrylate (PiBMA) and polystyrene (PS) of compositions, $PiBMA_{35}$-$Me_6Si_3O_2$-$PiBMA_{35}$, $PiBMA_{29}$-(n-$HexMeSi)_2O$-$PiBMA_{29}$, PS_{33}-$Me_6Si_3O_2$-PS_{33} and PS_{26}-(n-$HexMeSi)_2O$-PS_{26} by atom transfer radical polymerization (ATRP) approach. The composition of each polymer has been established by ^1H NMR and gel permeation chromatography studies. The polymers show a strong affinity for aggregation in selective solvents and adopt a spherical morphology in the size domain of 100-300 nm irrespective of the nature of the organic segments (PiBMA or PS). This approach has been utilized further to construct polymer-AuNP hybrid assemblies, featuring nano spherical morphologies.

विषय-सार

थीसिस में शामिल कार्य Au नैनोपार्टिकल (AuNP)-आधारित पिकरिंग इंटरफेसियल उत्प्रेरक (PICs) विकसित करने और माध्यमिक ऑर्गनॉसाईलेन्स के हाइड्रोलाइटिक ऑक्सीकरण के लिए उनके प्रयोग को, 1,1,3,3- टेट्राऑर्गनॉडायसाईलोक्ज़ेन्स, $(HRR^1Si)_2O$ (R, R^1 = अल्काइल / अराईल) के संश्लेषण के लिए एक व्यवस्थित अध्ययन प्रदान करता है। इस कार्य के दौरान, हमने दृश्य प्रकाश विकिरण के अंतर्गत AuNPs के सतह प्लास्मोन अनुनाद के उत्तेजना और इसके निहितार्थ से उत्पन्न प्लास्मोन प्रेरित फोटोथर्मल प्रभाव की जांच उत्प्रेरक प्रतिक्रियाओं के अध्ययन में की है। थीसिस को पांच अध्यायों में बांटा गया है। अध्याय I Si-H/ Si-vinyl/ Si-OH/ Si-OR समूह वाले रैखिक / चक्रीय ऑर्गनॉसाईलोक्ज़ेन्स के संश्लेषण और प्रतिक्रियाशीलता से सम्बंधित साहित्य का एक सिंहावलोकन प्रदान करता है। अध्याय II वर्तमान अध्ययन में अनुपालित कृत्रिम प्रक्रियाओं और चरित्रकरण विधियों के विस्तृत विवरण से संबंधित है।

अध्याय III में समाहित अध्ययन, AuNP-आधारित पिकरिंग इंटरफेसियल उत्प्रेरक बनाने के लिए एक सरल और व्यावहारिक दृष्टिकोण प्रदान करता है। विधि, क्लोरोफॉर्म में चक्रीय साईलोक्ज़ेन्स $[RSCH_2CH_2SiMeO]_4$, [R = CH_2CH_2OH (**1**); CH_2CH_2COOH (**2**)] से अनुबंधित AuNPs के प्रारंभिक संश्लेषण पर निर्भर करती है। इस कोलॉइडल विलयन में पानी मिलाने पर, AuNPs कार्बनिक परत से पानी-क्लोरोफॉर्म इंटरफ़ेस तक एक सहज चरण हस्तांतरण से गुजरते हैं। यह घटना क्लोरोफॉर्म में फैले गैर-कोलेसेंट पानी की बूंदों के गठन से स्पष्ट है। इस प्रकार बनाई गई द्विप्रावस्थिक व्यवस्थाओं को पिकरिंग इंटरफेसियल उत्प्रेरक, **PIC-1** और **PIC-2** के रूप में नामांकित किया गया है। अध्याय IV ऑर्गनॉसाईलेन्स के हाइड्रोलाइटिक ऑक्सीकरण की ओर पिकरिंग उत्प्रेरक की प्रभावकारिता पर एक विस्तृत अध्ययन के लिए समर्पित है। एक केस स्टडी के रूप में, मिथाइलफिनाइलसाईलेन ($MePhSiH_2$) की प्रतिक्रिया को 0.01 mol % Au (**PIC-1**) उत्प्रेरक के साथ परिस्थितियों में भिन्नता के अनुसार किया गया था: 25 डिग्री सेल्सियस (अंधेरा, परिवेश प्रकाश और 680 nm एलईडी स्रोत) और 80 डिग्री सेल्सियस (अंधेरा और परिवेश प्रकाश)। जबकि उत्प्रेरक 25 डिग्री सेल्सियस पर प्रकाश की अनुपस्थिति में निष्क्रिय पाया जाता है, प्रतिक्रिया परिवेश प्रकाश के साथ-साथ 680 nm एलईडी स्रोत के साथ रोशनी पर आसानी से बढ़ती है। उत्प्रेरक गतिविधि में एक उल्लेखनीय वृद्धि ऊँचे तापमान (80 डिग्री सेल्सियस) पर देखी गयी। नतीजे बताते हैं कि 25 डिग्री सेल्सियस पर AuNPs की गतिविधि को फोटो-प्रेरित घटना (फोटोथर्मल इफेक्ट) द्वारा बढ़ाया जाता है जो प्रकाश विकिरण के तहत AuNPs के प्लास्मोन उत्तेजना के परिणामस्वरूप होता है। यह अच्छी तरह से ज्ञात है कि प्लास्मोनिक उत्प्रेरण के अंतर्निहित तंत्र में अवशोषित ऊर्जा का गर्मी में कुशल रूपांतरण शामिल होता है, जिसके परिणामस्वरूप नैनोकणों के आसपास के तापमान में वृद्धि होती है। उत्प्रेरक को मुख्य उत्पाद 1,3-डायमिथाइल -1,3-डायफिनाइलडायसाईलोक्ज़ेन, $(HMePhSi)_2O$ के निर्माण के लिए चुनिंदा पाया जाता है, जबकि $MePhSi(OSiMePhH)_2$ मामूली राशि (<5%) में निर्मित होता है। विधि एक विस्तृत क्रियाधार व्यापकता प्राप्त करती है और विभिन्न 1,1,3,3- टेट्राऑर्गनॉडायसाईलोक्ज़ेन्स, $(HRR^1Si)_2O$, (R = Me, Ph; R^1 = Ph, *n*-Hex, *n*-Oct, cyclohexyl, $PhMe_2SiCH_2CH_2$, 2-$ThMe_2SiCH_2CH_2$; Th = thienyl) के संश्लेषण के लिए एक आशाजनक मार्ग प्रदान करती है। पिकरिंग इंटरफेसियल उत्प्रेरक **PIC-2** उत्प्रेरक घटना के दौरान अपेक्षाकृत कम स्थिर है। अनुवर्ती अध्ययन में, हमने हाइड्रोसिलाइलेशन

की दिशा में $(HMePhSi)_2O$ और $(HPh_2Si)_2O$ की प्रतिक्रियाशीलता की जांच की है, साथ ही उपयुक्त क्रियाधार के साथ डीअल्काईलेटिव युग्मन प्रतिक्रियाएं भी की हैं। इस अध्ययन से सिलिकॉन परमाणुओं पर अलग-अलग प्रतिस्थापनों वाले कार्यात्मक-प्रतिस्थापित डायसाईलोक्ज़ेन्स के साथ-साथ रैखिक ओलिगोसाईलोक्ज़ेन्स का संश्लेषण हुआ है। अध्याय V में प्रस्तुत किया गया कार्य साईलोक्ज़ेन-संशोधित पॉलीआइसोबोरनायलमेथएक्राइलेट (PiBMA) और पॉलीस्टाइरीन (PS) की रचनाओं [$PiBMA_{35}$-$Me_6Si_3O_2$-$PiBMA_{35}$, $PiBMA_{29}$-(n-$HexMeSi)_2O$-$PiBMA_{29}$, PS_{33}-$Me_6Si_3O_2$-PS_{33} and PS_{26}-(n-$HexMeSi)_2O$-PS_{26}] का परमाणु हस्तांतरण तत्वरूप बहुलककरण (ATRP) पद्धति द्वारा संश्लेषण से संबंधित है। प्रत्येक बहुलक की संरचना ^1H नाभिकीय चुम्बकीय अनुनाद (NMR) और जेल पारगम्य क्रोमैटोग्राफी (GPC) अध्ययन द्वारा स्थापित की गई है। बहुलक चुनिंदा विलायकों में एकत्रीकरण के लिए एक मज़बूत आत्मीयता दिखाते हैं और कार्बनिक सेगमेंट (PiBMA या PS) की प्रकृति से निरपेक्ष होकर, 100-300 nm के आकार अनुक्षेत्र में एक गोलाकार रूपरेखा अपनाते हैं। इस पद्धति का उपयोग बहुलक-AuNP संकर-समूहों के निर्माण के लिए किया गया है जो नैनो गोलाकार आकृतियों को दर्शाती हैं।

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GLOSSARY OF SYMBOLS AND ABBREVIATIONS

%	percent
δ	chemical shift
ν	frequency
°C	degree centigrade
λ_{max}	absorption maxima
AuNPs	gold nanoparticles
ATR	attenuated total reflectance
ATRP	atom transfer radical polymerization
b. p.	boiling point
bcp	block copolymer
br	broad
n-Bu	*n*-butyl
n-BuLi	*n*-butyl lithium
t-Bu	*tert*-butyl
cyclo-Hex	cyclohexyl
cm	centimeter
d	doublet
DLS	dynamic light scattering
DEPT	distortionless enhancement by polarization transfer
DSC	Differential scanning calorimetry
ESI	electrospray ionization
Et	ethyl
FESEM	Field emission scanning electron microscopy
FT	Fourier transform
g	gram
GC	gas chromatography
GPC	gel permeation chromatography
h	hour
Hz	Hertz
HPLC	high performance liquid chromatography
HRTEM	High resolution transmission electron microscopy

BFTEM	Bright field transmission electron microscopy
n-Hex	*n*-hexyl
IR	infrared
J	coupling constant
k	rate constant
m	multiplet
m/z	mass/ charge
MHz	megahertz
M^+	molecular ion
Me	methyl
mmol	millimole
mol	mole
mL	milliliter
M_n	number average molecular weight
M_w	weight average molecular weight
nm	nanometer
NMR	nuclear magnetic resonance
OAc	acetate
PDI	polydispersity index
Ph	phenyl
PiBMA	poly(isobornylmethacrylate)
PS	polystyrene
PDMS	poly(dimethylsiloxane)
PMDETA	*N, N, N', N'', N''*- pentamethyldiethylenetriamine
PIC	Pickering interfacial catalyst
q	quartet
ROP	ring opening polymerization
s	singlet
LSPR	localized surface plasmon resonance
t	triplet
TEM	transmission electron microscopy
Th	thienyl
T_g	glass transition temperature

TGA	thermogravimetric analysis
THF	tetrahydrofuran
TMS	tetramethylsilane
TON	turn over number
TOF	turn over frequency
UV	ultraviolet
wt	weight
RT	room temperature